(12)   **EUROPEAN PATENT APPLICATION**

(54) Method of forming a magnetic layer on a substrate.

(57) A monolayer magnetic coating is prepared by applying magnetic particles which have an electrostatic charge in an aqueous environment to an active layer on a substrate, the active layer having an electrostatic charge in an aqueous environment opposite to the charge on the magnetic particles so that the particles bond to the active layer. The magnetic particles are dispersed in an electrolyte (eg Na Cl) and the concentration of the electrolyte is adjusted to reduce the coulombic repulsive forces between the particles, permitting them to move closer together and thereby increasing the magnetic particle packing density in the resultant magnetic coating.

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METHOD OF FORMING A MAGNETIC LAYER
ON A SUBSTRATE

This invention relates to a method of forming a magnetic layer on a substrate.

In the preparation of magnetic recording materials, such as for magnetic disks and tapes, it has been common to use magnetic particles, such as gamma Fe_2O_3, dispersed in a binder mixture to form the magnetic recording material. A dispersion is usually formed by milling the ingredients together for an extended period of time in an effort to thoroughly coat the magnetic particles with the binder ingredients and to break up collections or aggregations of such particles. Magnetic particles of this type tend to cling together and it is desirable to reduce or eliminate this aggregation of particles in order to produce smaller effective magnetic particle sizes for higher density magnetic recording. The degree of uniform dispersion of the magnetic particles in the binder is an important factor in determining the final quality of the magnetic coating, as measured by the parameters of surface smoothness, orientation ratio, signal-to-noise ratio, off-track performance, modulation noise, coercive force and wear properties.

After filtering, this dispersion is coated onto a substrate by spin coating, dip coating, spray coating or doctor blade (gravure) coating. The magnetic particles in the wet coating are then magnetically aligned by moving the coated substrate past a magnetic field. The coating is then cured to improve hardness and durability. The cured magnetic coating may be ground to reduce the coating thickness and then buffed to reduce surface roughness.

In order to increase the recording areal density, the coating thickness has to be reduced. Mechanical grinding to less than 5000 $\overset{o}{A}$ is difficult, if not beyond the limit of present technology. Also, as the coating thickness is reduced, the signal amplitude is decreased and this presents a major problem. New, higher moment particles and a higher

pigment volume concentration (PVC) are needed. PVC may be defined as
the percentage of magnetic material in the coating relative to the total
volume of the binder material and the volume of the magnetic material.
The PVC of current magnetic coatings is about 20-30%, and it is
difficult to increase this and still maintain the rheological properties
of the organic dispersion.

US-A-4,333,961 discloses a process for producing a magnetic coating
having a high PVC and good magnetic orientability. In that process, a
so-called charged "active" layer is produced on a suitable disk
substrate and magnetic particles having a charge opposite to that of the
active layer are brought into contact with the active layer. The
magnetic particles are coated with colloidal silica to reduce the
tendency of the particles to agglomerate, as taught in US-A-4,280,918.

Practice of the present invention leads to an increase in the
concentration of magnetic particles in a magnetic coating produced using
the process of US-A-4,333,961.

A method of forming a magnetic layer on a substrate comprising
coating said substrate with an active coating material having an
electrostatic charge to form an active layer, applying to the active
coating material magnetic particles coated with colloidal silica, the
silica-coated magnetic particles having an electrostatic charge thereon
in an aqueous environment opposite to the charge on said active coating
material, whereby the magnetic particles are electrostatically attracted
to and bonded to said active material to form a magnetic layer, is
characterised, according to the invention, by the silica-coated magnetic
particles being dispersed in an electrolyte and by adjusting the
concentration of said electrolyte to reduce the coulombic repulsive
forces between adjacent silica-coated magnetic particles to permit
closer spacing between the magnetic particles.

As in the process described in US-A-4,333,961, the magnetic particles are first treated with HCl to facilitate the separation of aggregated particles. The acid is then removed and the particles are dispersed ultrasonically at pH = 3.5. A colloidal silica dispersion in water (approximately 70 $\overset{\circ}{A}$ particles) is prepared and the pH of this dispersion is adjusted to 3.5 as taught in US-A-4,280,918. At this pH, silica has a negative surface charge and gamma Fe_2O_3 or Co doped gamma Fe_2O_3 has a positive surface charge. By injecting an excess of such negatively charged colloidal silica particles into an ultrasonic flow cell containing the dispersion of positively charged gamma Fe_2O_3, the colloidal silica particles encapsulate the gamma Fe_2O_3, as discussed extensively in the aforementioned US-A-4,280.918. The dispersion consists of colloidal silica-coated gamma Fe_2O_3, which has a negative surface charge when the pH is higher than 2.5.

The present invention is employed to attenuate the coulombic repulsion between the silica coated particles in such a way that the mean particle separation is decreased, but aggregation does not occur. As a result, these particles can be deposited on a disk with a high packing density without losing the advantage of a stable and well dispersed system.

This principle is best understood when considering the interaction energy of the colloidal particles in the presence of an electrolyte:-

$$U_{total} = U_{mag} + U_{el} + U_{vw}$$

In a stable system the attractive magnetic interaction ($U_{mag} \sim 1/r^3$) and van der Waal's interaction ($U_{vw} \sim A/r^6 - B/r^{12}$) are counterbalanced by the repulsive coulombic interaction ($U_{el} \sim exp-[-\kappa r]$) between the double layers of the charged particles (r = particle separation). The spatial extent of this repulsive force is determined by the Debye-Hückel screening length $1/\kappa$, where κ is given by

$$\kappa^2 = 4\pi/K_B T \varepsilon \Sigma_i n_i z_i^2 e^2$$

where ε = dielectric constant, K_B = Boltzman constant,
T = temperature, n = concentration of electrolyte,
z = valence of ions, and e = electrical charge.

Therefore, by increasing the electrolyte concentration, the screening length κ^{-1} decreases and consequently reduces the repulsive interaction between particles at a given particle separation. Applying this principle to the coating process of the aforementioned US-A-4,333,961, the concentration of an electrolyte (such as sodium chloride) in an aqueous dispersion of magnetic particles is adjusted to a desired value. Subsequently, a disk substrate already coated with an active layer, is exposed to a solution of the same electrolyte to ensure an identical ionic environment for particles and disk surface. As the coating is deposited on the disk, a magnetic field is applied thereto to magnetically align the magnetic particles in the desired direction.

After coating, the disk is spray washed with distilled water to remove any excess magnetic particles.

Following the procedure of the present invention, gamma Fe_2O_3 particles were deposited on polymer coated glass slides at various electrolyte concentrations. The polymer coat consisted of partially cured polyamide (Versamid - General Mills) and epoxy (Epon - Shell) capable of generating a positively charged interface in electrolyte systems.

The obtained data in Table I below shows that at higher electrolyte levels the number of particles or pigment volume concentration (PVC) increased approximately by 40% as compared with systems having low electrolyte concentrations.

Electrolyte Concentration (mols/liter)	$<10^{-5}$	1×10^{-5}	1×10^{-4}	2×10^{-3}
Magnetic moment $\times 10^4$ (emu/cm^3)	73.3	77.6	77.6	105.6

Electrolyte Concentration (mols/liter)	6×10^{-3}	1×10^{-2}	5×10^{-1}
Magnetic moment $\times 10^4$ (emu/cm^3)	111.2	107.5	110.6

Table I

The particle number per area was measured using a vibrating sample magnetometer (VSM) and the results in emu units/cm^3 are directly proportional to the volume of magnetic material. In addition, several (25) disks were prepared using the process of US-A-4,333,961. The average moment of those disks (13) prepared in the presence of 1×10^{-2} mols/liter NaCl electrolyte was measured at 1.6×10^{-1} emu/cm^3, and in the absence of electrolyte (12 disks) only at 8×10^{-2} emu/cm^3. The considerably higher PVC of these disks as compared to the results in Table I may be attributed to a magnetic field gradient which tends to concentrate particles prior to their interaction with a positively charged polymer layer. The higher PVC in those disks prepared in the presence of 1×10^{-2} mols/liter NaCl electrolyte is strikingly visible when observing the coating under the scanning electron microscope.

Further, static as well as dynamic magnetic measurements show that the increase in moment and signal amplitude are achieved without

degrading either the orientation ratio or the frequency resolution of the final disk.

Although the data above related to rigid disks, it will be understood that the invention may also be applied to the formation of magentic layers on flexible disks and tape.

CLAIMS

1.   A method of forming a magnetic layer on a substrate comprising coating said substrate with an active coating material having an electrostatic charge to form an active layer, applying to the active coating material magnetic particles coated with colloidal silica, the silica-coated magnetic particles having an electrostatic charge thereon in an aqueous environment opposite to the charge on said active coating material, whereby the magnetic particles are electrostatically attracted to and bonded to said active material to form a magnetic layer the method being characterised by the silica-coated magnetic particles being dispersed in an electrolyte and by adjusting the concentration of said electrolyte to reduce the coulombic repulsive forces between adjacent silica-coated magnetic particles to permit closer spacing between the magnetic particles.

2.   A method as claimed in claim 1, including the step of applying a magnetic field to the silica-coated magnetic particles as they are applied to said active layer to magnetically align the particles.

3.   A method as claimed in claim 1 or claim 2, in which said electrolyte concentration is at least 10^{-5} mols per liter.

4.   A method as claimed in claim 3, in which said electrolyte concentration is between 10^{-5} and 5×10^{-1} mols per liter.

5.   A method as claimed in any preceding claim, in which said electrolyte contains sodium chloride.

European Patent Office

EUROPEAN SEARCH REPORT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

DOCUMENTS CONSIDERED TO BE RELEVANT | EP 83106325.0

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X,D	US - A - 4 333 961 (BRUCE) * Claims 1-15; column 2, lines 22-31; column 1, lines 31-40 *	1,2	G 11 B 5/84
A,D	US - A - 4 280 918 (HOMOLA) * Abstract; claims 1-7 *	1	
A	DE - A1 - 2 808 144 (IBM) * Claim 2 *	5	
A	US - A - 2 885 366 (ILER) * Fig. 1-5; claims 1-12 *	1	

TECHNICAL FIELDS SEARCHED (Int Cl ³)

G 11 B 5/00

B 01 J 13/00

B 05 D 1/00

H 01 F 41/00

C 09 D 5/00

The present search report has been drawn up for all claims

Place of search VIENNA	Date of completion of the search 16-11-1983	Examiner BERGER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, r after the filing date
D : document cited in the application
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